UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Solution properties of polymers

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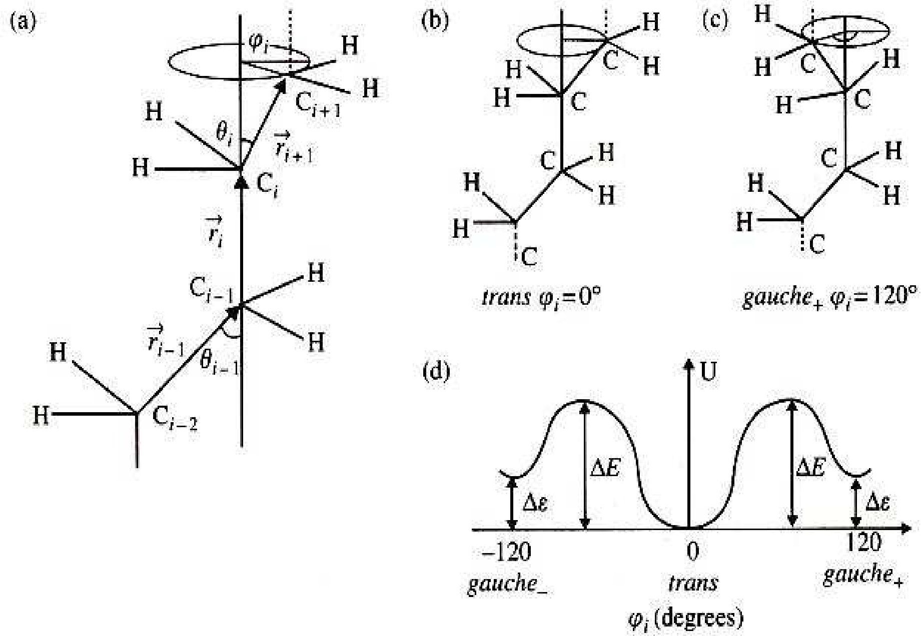
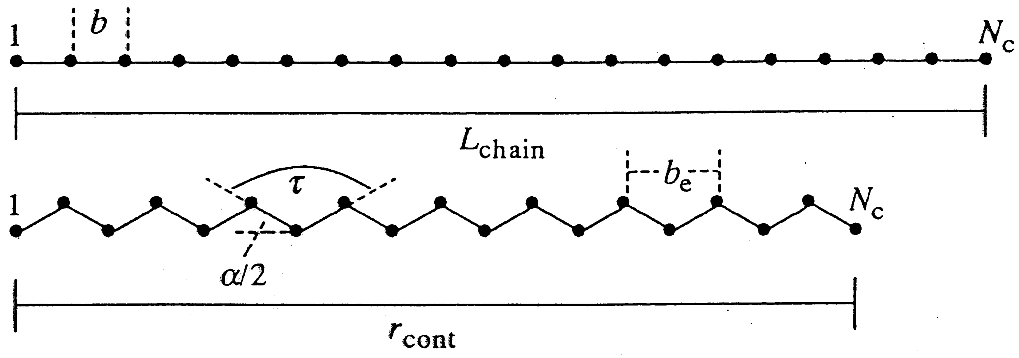
Solution properties of polymers

- Properties of ideal polymer chain
- Thermodynamics of mixing (binary systems containing polymers)
- Osmotic pressure
- Interactions in dilute solutions
- Properties of real polymer chain
- Viscosity
- Light scattering

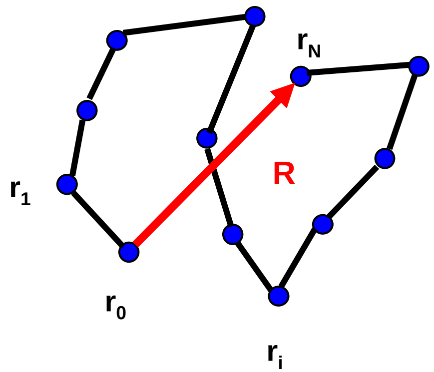
Properties of ideal polymer chain

Thermal motion of molecules: translation
rotation
intramolecular rotation





End-to-end distance



$$\langle R^2 \rangle \equiv \langle (r_N - r_0)^2 \rangle = \left\langle \sum_{i=1}^{n} \vec{l}_i \sum_{j=1}^{n} \vec{l}_j \right\rangle = Nl^2 + 2\sum_{i=1}^{n} \sum_{j\neq i}^{n} \langle \vec{l}_i \vec{l}_j \rangle$$

$$\langle \vec{l}_i \vec{l}_j \rangle = l^2 \langle \cos\alpha_{ij} \rangle$$

Freely jointed chain

$$\langle R^2 \rangle = Nl^2$$

$$\lim_{|i-j|\to\infty} \langle \cos\alpha_{ij} \rangle = 0$$

$$\langle R^2 \rangle = l^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \cos\alpha_{ij} \rangle = l^2 \sum_{i=1}^{N} C_i^{'} = C_n N l^2$$

Flory's characteristic ratio C_∞

$$\langle R^2 \rangle \cong C_\infty N l^2$$

Polymer	Structure	C_∞	b (Å)	ρ ($g\,cm^{-3}$)	M_0 ($g\,mol^{-1}$)
1,4-Polyisoprene (PI)	$-(CH_2CH{=}CHCH(CH_3))-$	4.6	8.2	0.830	113
1,4-Polybutadiene (PB)	$-(CH_2CH{=}CHCH_2)-$	5.3	9.6	0.826	105
Polypropylene (PP)	$-(CH_2CH_2(CH_3))-$	5.9	11	0.791	180
Poly(ethylene oxide) (PEO)	$-(CH_2CH_2O)-$	6.7	11	1.064	137
Poly(dimethyl siloxane) (PDMS)	$-(OSi(CH_3)_2)-$	6.8	13	0.895	381
Polyethylene (PE)	$-(CH_2CH_2)-$	7.4	14	0.784	150
Poly(methyl methacrylate) (PMMA)	$-(CH_2C(CH_3)(COOCH_3))-$	9.0	17	1.13	655
Atactic polystyrene (PS)	$-(CH_2CHC_6H_5)-$	9.5	18	0.969	720

Equivalent freely jointed chain

Contour lenght

$$nl = R_{\max}$$

Equality of the mean-square end-to-end distance

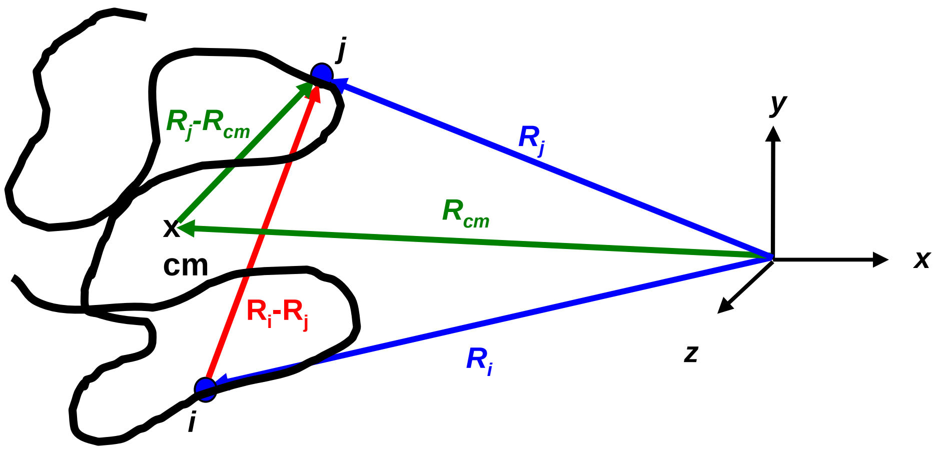
$$\langle R^2 \rangle = nb^2 = bR_{\max} = C_\infty N l^2$$

$$n = \frac{R_{\max}^2}{C_\infty N l^2} \qquad b = \frac{\langle R^2 \rangle}{R_{\max}} = \frac{C_\infty N l^2}{R_{\max}}$$

Freely rotating chain

$$\langle R^2 \rangle = Nl^2 + 2Nl^2 \frac{\cos\theta}{1-\cos\theta} = Nl^2 \left(\frac{1+\cos\theta}{1-\cos\theta} \right)$$

Radius of gyration



Definition $$\vec{R}_g^{\,2} \equiv \frac{1}{N}\sum_{i=1}^{N}\left(\vec{R}_i - \vec{R}_{cm}\right)^2$$

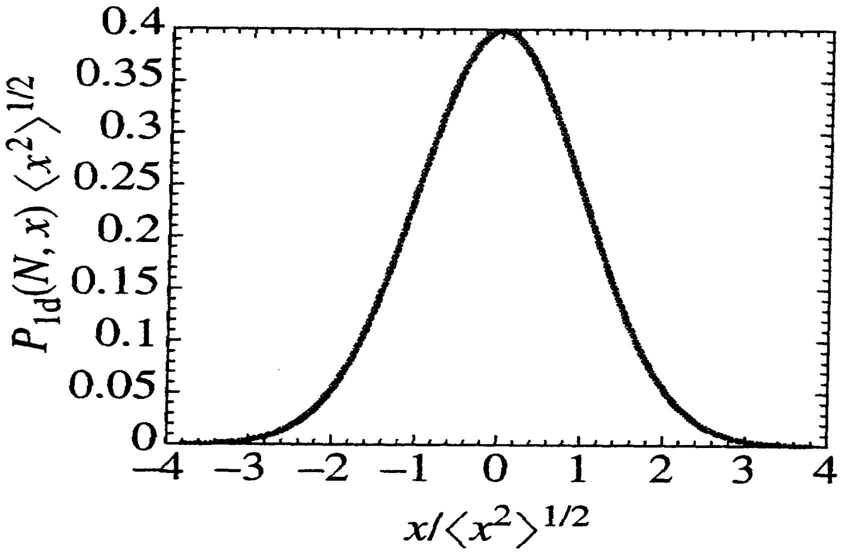
Relation between radius of gyration and end-to-end distance

$$\left\langle R_g^2 \right\rangle = \frac{b^2 N}{6} = \frac{\left\langle R^2 \right\rangle}{6}$$

Distribution of end-to-end vectors

Model random walk

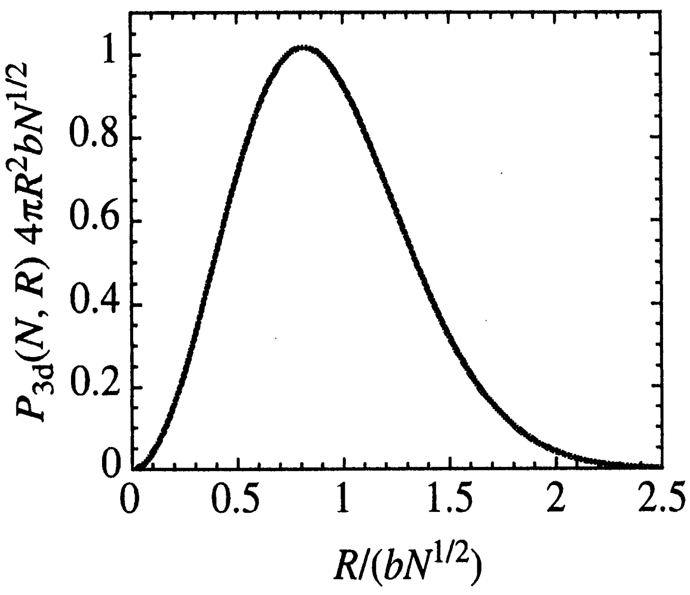
$$P_{1d}(N, x) = \frac{1}{\sqrt{2\pi\langle x^2 \rangle}} \exp\left(-\frac{x^2}{2\langle x^2 \rangle}\right)$$



Normalized one-dimensional Gaussian probability distribution function for occupaying position *x* after random *N* steps from origin x=0

Three-dimensional distribution function

$$P_{3d}(N,R)4\pi R^2 dR = 4\pi\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\exp\left(-\frac{3R^2}{2Nb^2}\right)R^2 dR$$



Normalized distribution function of end-to-end distances for an ideal linear chain

Free energy of an ideal chain

$$S = k \ln \Omega \qquad S\left(N, \vec{R}\right) = -\frac{3}{2} k \frac{\vec{R}^2}{Nb^2} + S\left(N, 0\right)$$

Helmholtz free energy of the streched chain

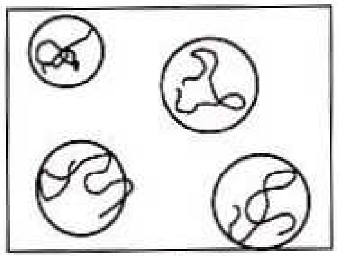
$$F\left(N,\vec{R}\right)=\frac{3}{2}kT\frac{\vec{R}^2}{Nb^2}+F\left(N,0\right)$$

Deformation force

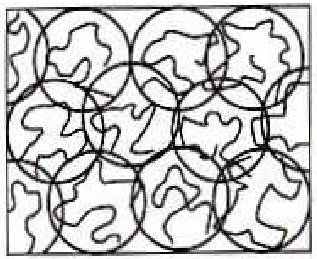
$$\vec{f}=\frac{3kT}{Nb^2}\vec{R}$$

Dependence on temperature and number of segments

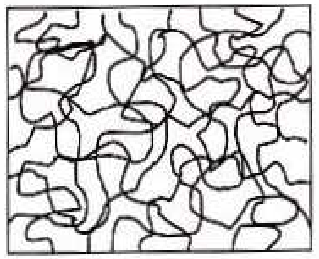
Polymer solutions



Dilute ($\phi < \phi^*$)



Overlap ($\phi = \phi^*$)



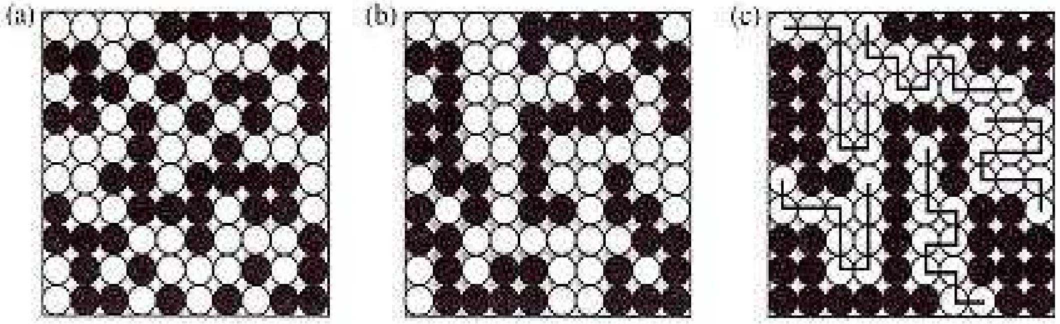
Semidilute ($\phi > \phi^*$)

$$\varphi^* = \frac{NV_0}{V}$$

$$c^* = \frac{\rho N V_0}{V}$$

Thermodynamics of mixing

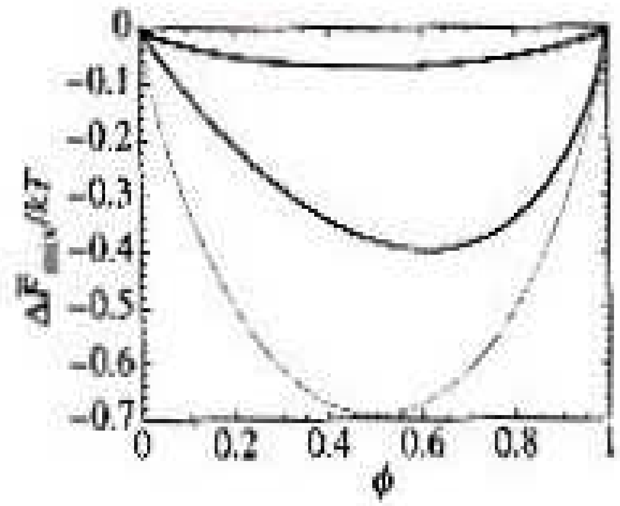
Flory's lattice model



Entropy of mixing

$$\Delta\bar{S}_{mix} = k\left[\frac{\varphi_A}{N_A}\ln\varphi_A + \frac{\varphi_B}{N_B}\ln\varphi_B\right]$$

$$\Delta\bar{F}_{mix} = -T\Delta\bar{S}_{mix} = kT\left[\frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi)\right]$$



The mixing free energy of an ideal mixture is always favourable (negative) and all composition are stable. The bottom curve is a regular solution with $N_A = N_B = 1$. The middle curve is a polymer solution with $N_A = 10$ and $N_B = 1$. The top curve is a polymer blend with $N_A = N_B = 10$.

Energy of mixing

$$\Delta \overline{U}_{mix} = \frac{z}{2}\phi(1-\phi)(2u_{AB} - u_{AA} - u_{BB})$$

Flory's interaction parameter χ

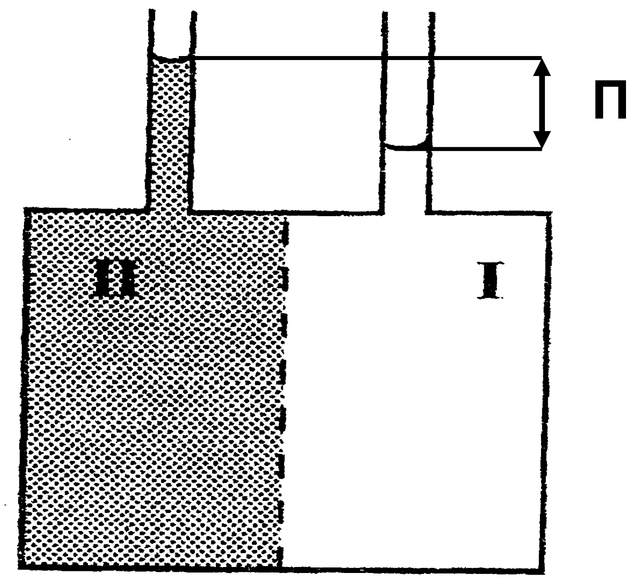
$$\chi \equiv \frac{z}{2}\frac{(2u_{AB} - u_{AA} - u_{BB})}{kT}$$

$$\Delta \overline{F}_{mix} = \Delta \overline{U}_{mix} - T\Delta \overline{S}_{mix} = kT\left[\frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi) + \chi\phi(1-\phi)\right]$$

Temperature dependence of χ

$$\chi(T) \cong A + \frac{B}{T}$$

Osmotic pressure



I solvent

II solution

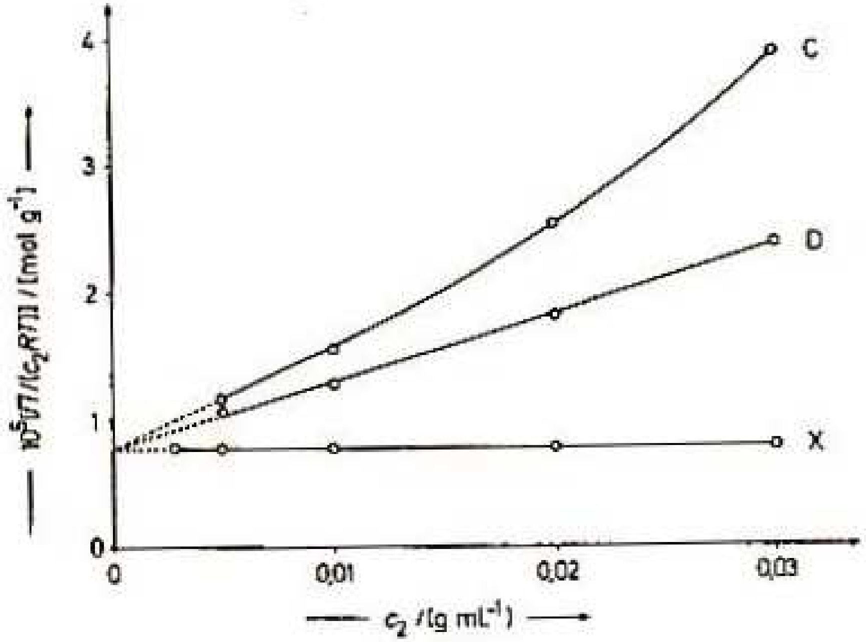
Definition of osmotic pressure

$$\Pi \equiv -\left(\frac{\partial \Delta F_{mix}}{\partial V}\right)_{n_A}$$

$$\Pi = \frac{kT}{b^3}\left[\frac{\phi}{N_A} + (1-2\chi)\frac{\phi^2}{2} + \ldots\right]$$

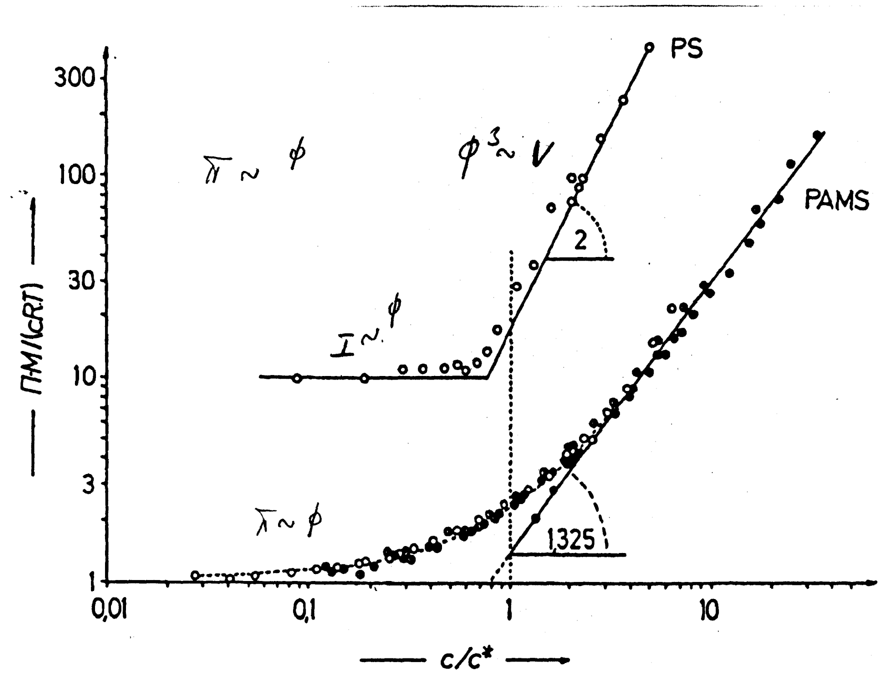
$$\Pi = RT\left(\frac{c}{M} + A_2 c^2 + \ldots\right)$$

$$A_2 = \frac{v N_{Avo}}{2M^2} \approx 1 - 2\chi \approx \frac{T-\Theta}{T}$$



Concentration dependence of reduced osmotic pressures of a poly(methyl methacrylate) in various solvents at 20℃ (1). X – m-xylene is Θ solvent ($A_2 = 0$), 1,4-dioxane D leads to a positive second virial coefficient $A_2 > 0$ (good solvent), and chloroform C furnishes both second and third virial coefficients. The common intercept at $c_2 \to 0$ equals $1/M_n$

Good solvent $A_2 > 0$; θ *solvent* $A_2 = 0$; bad solvent $A_2 < 0$



Dependence of reduced osmotic pressures, (*ΠM/cRT)*, on normalized overlap concentration *c/c (*c** from viscosity) for polystyrenes PS in the *Θ*-solvent cyclohexane at 34 °C and poly(α-methylstyrene)s PAMS in the good solvent toluene at 25 °C(2). The osmotic overlap concentration is at $c_{\Pi}^* = c_v^*$.**

Properties of a real polymer chain in a good solvent

Swelling of polymer coil due to osmotic pressure

$$F_{\mathrm{int}} \approx kTv\frac{N^2}{R^3}$$

Total energy

$$F = F_{\mathrm{int}} + F_{ent} \approx kT\left(v\frac{N^2}{R^3} + \frac{R^2}{Nb^2}\right)$$

Equilibrium state

$$\frac{\partial F}{\partial R} = 0 = kT\left(-3\frac{N^2}{R_F^4} + 2\frac{R_F}{Nb^2}\right)$$

$$R_F^5 \approx vb^2N^3$$

$$R_F \approx v^{\frac{1}{5}}b^{\frac{2}{5}}N^{\frac{3}{5}}$$

Expansion coefficient

$$\alpha = \frac{R_F}{bN^{1/2}} \approx \left(\frac{v}{b^3}N^{1/2}\right)^{1/5} \approx z^{1/5}$$

Flory – Fox equation

$$\alpha^2 \equiv \frac{\langle \boldsymbol{R}^2 \rangle}{\langle \boldsymbol{R}_0^2 \rangle}$$

$$\alpha^5 - \alpha^3 = \mathbf{1.276}\boldsymbol{z}$$

Viscosity

Increase of solution viscosity caused by polymer dissolved

$$\eta = \eta_0 (1 + 2.5\phi) = \eta_0 \left(1 + 2.5 \frac{V_{pol} c}{M} \right)$$

Definition of the intrinsic viscosity

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0} \frac{1}{c} \approx \frac{V_{pol}}{M}$$

Relation between intrinsic viscosity and critical overlap concentrtion

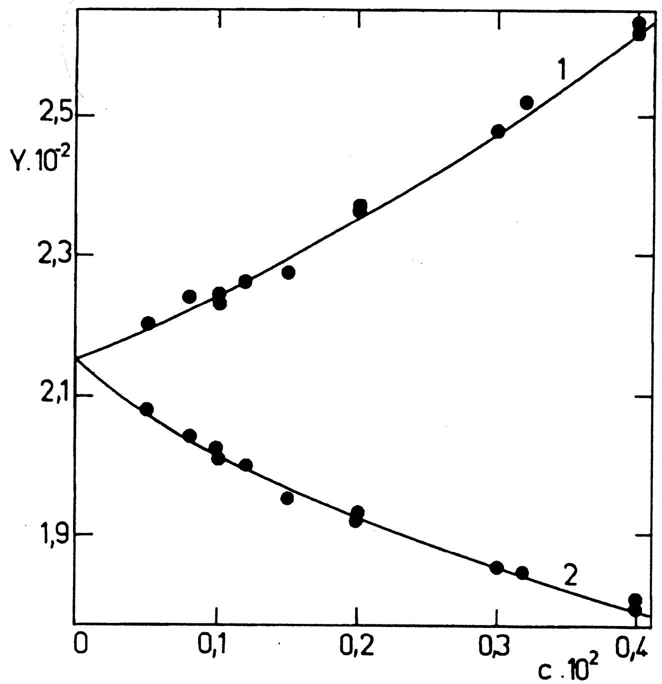
$$[\eta] \approx \frac{V_{pol}}{M} \approx \frac{R^3}{M} \approx \frac{1}{c^*}$$

Huggins equation

$$\frac{\eta - \eta_0}{\eta_0 c} = [\eta] + k_H [\eta]^2 c + \ldots$$

Kraemer equation

$$\frac{\ln(\eta/\eta_0)}{c} = [\eta] + \left(k_H - \frac{1}{2}\right)[\eta]^2 c + \ldots$$



Determination of the intrinsic viscisity for polymethylmetacrylate in benzene at 25 ℃. 1 - Huggins plot 2 - Kraemer plot that extrapolate to the intrinsic viscosity at zero concentration.

Dependence of intrinsic viscosity on molar mass $[\eta] = KM^{a}$

Light scattering

Intensity of light scattered by one small particle

$$\frac{I}{I_0} = \frac{16\pi^4}{\lambda^4 r^2}\alpha^2$$

Intensity of light scattered by dilute gas

$$\frac{\bar{I}}{I_0} = \frac{4\pi^2 n^2}{\lambda^4 r^2}\left(\frac{dn}{dc}\right)^2 \frac{cM}{N_{Avo}}$$

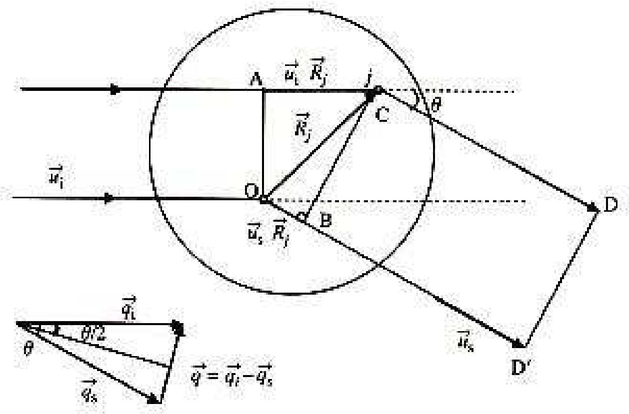
Rayleigh ratio

$$R_\theta = \frac{\bar{I} r^2}{I_0} = \frac{4\pi^2 n^2}{\lambda^4}\left(\frac{dn}{dc}\right)^2 \frac{cM}{N_{Avo}} = KcM$$

Role of concentrations fluctuations

$$\frac{Kc}{R_\theta} = \frac{1}{RT}\left(\frac{\partial \Pi}{\partial c}\right)_T = \frac{1}{M} + 2A_2 c + \ldots$$

Light scattering by large particles



Phase shift

$$\varphi_j = \frac{2\pi n}{\lambda}\left(\vec{u}_i - \vec{u}_s\right)\vec{R}_j = \left(\vec{q}_i - \vec{q}_s\right)\vec{R}_j = \vec{q}\vec{R}_j$$

Scattering wave vector

$$q \equiv \left|\vec{q}\right| = 2\left|\vec{q}_i\right|\sin\left(\frac{\theta}{2}\right) = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

Form function

$$P\left(\vec{q}\right) \equiv \frac{I_s\left(\vec{q}\right)}{I_s\left(0\right)}$$

$$P\left(q\right) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\sin\left(qR_{ij}\right)}{qR_{ij}}$$

$$P\left(q\right) = 1 - \frac{16\pi^2 n^2}{3\lambda^2}\left\langle R_g^2\right\rangle \sin^2\left(\frac{\theta}{2}\right) + \ldots$$

$$\left(\frac{Kc}{R_\theta}\right)_{c\to 0} = \frac{1}{M_w}\left[1+\frac{16\pi^2 n^2}{3\lambda}\left\langle R_g^2\right\rangle \sin^2\left(\frac{\theta}{2}\right)+\ldots\right]$$

The presentation is based on the book *Polymer physics* by M. Rubinstein and R.H. Colby, Oxford University Press Inc., New York, 2003

1) **G.V.Schulz, H. Doll, Ber. Deutch. Chem. Ges. 80, (1947), 232**
2) **P. Štěpánek, K. Perzynski, M. Delsanti, M. Adam, Macromolecules 17, (1984), 2340**

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